



Highly-controllable imprinted polymer nanoshell at the surface of silica nanoparticles based room-temperature phosphorescence probe for detection of 2,4-dichlorophenol



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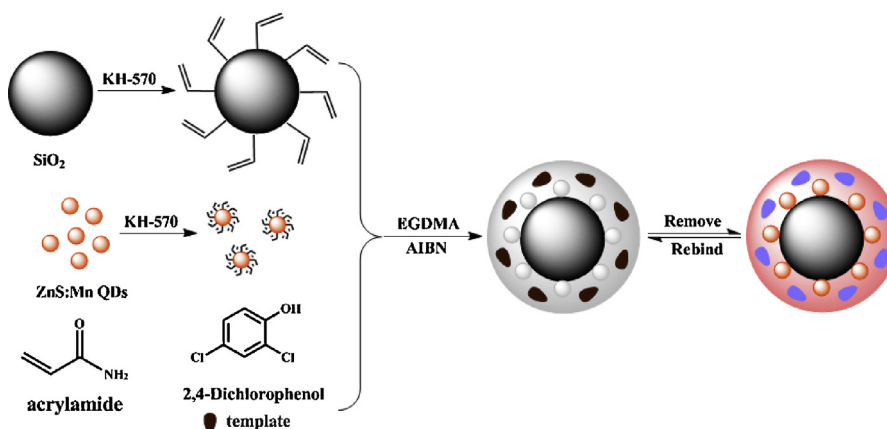
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HIGHLIGHTS

- Highly-controllable core–shell MIPs@SiO₂–ZnS:Mn QDs were prepared.
- The MIPs@SiO₂–ZnS:Mn QDs integrated the advantages of molecular imprinting and QDs.
- We used MIPs@SiO₂–ZnS:Mn QDs as phosphorescence probes for detection of 2,4-DCP.
- MIPs@SiO₂–ZnS:Mn QDs were successfully applied to detect 2,4-DCP in real samples.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper reports a facile and general method for preparing an imprinted polymer thin shell with Mn-doped ZnS quantum dots (QDs) at the surface of silica nanoparticles by stepwise precipitation polymerization to form the highly-controllable core–shell nanoparticles (MIPs@SiO₂–ZnS:Mn QDs) and sensitively recognize the target 2,4-dichlorophenol (2,4-DCP). Acrylamide (AM) and ethyl glycol dimethacrylate (EGDMA) were used as the functional monomer and the cross-linker, respectively. The MIPs@SiO₂–ZnS:Mn QDs had a controllable shell thickness and a high density of effective recognition sites, and the thickness of uniform core–shell 2,4-DCP-imprinted nanoparticles was controlled by the total amounts of monomers. The MIPs@SiO₂–ZnS:Mn QDs with a shell thickness of 45 nm exhibited the largest quenching efficiency to 2,4-DCP by using the spectrofluorometer. After the experimental conditions were optimized, a linear relationship was obtained covering the linear range of 1.0–84 μmol L⁻¹ with a correlation coefficient of 0.9981 and the detection limit (3σ/k) was 0.15 μmol L⁻¹. The feasibility of the developed method was successfully evaluated through the determination of 2,4-DCP in real samples. This study provides a general strategy to fabricate highly-controllable core–shell imprinted polymer-contained QDs with highly selective recognition ability.

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1. Introduction

Molecular imprinting [1,2], as a versatile and well-established technique, which is widely used for synthesizing molecularly imprinted polymers (MIPs) with specific molecular recognition properties, has attracted much attention in recent years [3,4]. The synthetic process is based on the copolymerization of functional monomers and cross-linkers to form complexes with the template molecules, after the removal of the template, the special tailor-made binding sites that are complementary in size shape and functionality to template are obtained [5–9]. Due to the desired predetermination, high specific selectivity and practicability, MIPs have been widely used in various significant applications, such as chemical sensor [10–12], extraction and separation [13–15], catalysis [16–18], drug delivery and controlled release [19–21] and so on. However, the bulk MIPs exhibit high selective recognition but have the poor binding capacity, low binding kinetics and shortcomings of incomplete template. This is due largely to the extraction of template molecules embedded inside the thick polymer network is quite difficult [22]. To overcome those shortcomings, the surface molecular imprinting technique has been developed in recent years and a series of convenient and controllable methods have been explored by several research groups [23–26]. Core-shell structural surface imprinted polymers are used efficiently to improve the binding kinetics, binding capacity, and site accessibility to the target molecules. In addition, functional materials can be easily combined into the imprinted shell layers for various applications due to the independent internal core [27].

Recently, quantum dots (QDs) have been widely used as probes for recognizing and sensing different kinds of analytes including ions [28], small molecules [29–31], and biological macromolecule [32] due to their excellent advantages, such as high luminescence efficiency, size-dependent emission wavelengths, narrow symmetric emission and excellent photostability [33,34]. To our knowledge, most of the detection methods are based on the fluorescence properties, and there are only a few studies on using of the phosphorescence properties. Room temperature phosphorescence (RTP) as an effective detection mode has become a hotspot due to its fascinating advantages over fluorescence [35]. The QDs with phosphorescence have longer lifetime, which can allow an appropriate delay time and avoid the interferences from autofluorescence and scattering light [36]. It is for this reason that RTP QDs detection shows very famous reliability. Therefore, the RTP detections based on QDs is a topic of great interest. However, traditional RTP detections are faced with a difficult problem that is the interference of the coexisting substances. To improve further the selectivity of QDs-based RTP sensor, a promising way is to combine the RTP optosensing with the MIPs. Until now, few protocols have been developed to construct the MIPs-based RTP materials (QDs). For example, Wang et al. have prepared a type of MIPs-based Mn-doped ZnS QDs for RTP detection of pentachlorophenol in water [37]. Tan et al. have developed a new strategy for producing phosphorescent MIPs for specific recognition of a target protein [38]. Our group has reported the surface molecular imprinting on Mn-doped ZnS QDs for detecting 2,4,5-trichlorophenol [39]. In a word, the high sensitivity of RTP optosensing of the QDs combines with the advantages of highly selective MIPs can analyze trace substances in real samples and reduce the limit of detection.

Chlorophenols (CPs), as a group of phenolic compounds, are often found in the waste discharges produced by chemical industries, such as plastics, petroleum refineries, wood preservers, pesticides, biocides, pulp, and insulation materials [40–42]. The United States Environmental Protection Agency (US EPA) has listed chlorophenols as pollutants due to their suspected carcinogenicity, strong odor emission, bio-accumulation, recalcitrance, high toxicity, and mutagenicity to living organisms [43,44].

2,4-Dichlorophenol (2,4-DCP), a typical chlorophenols, can cause itch, faint, anemia, comedo and has been linked with the appearance of cancer [45,46]. Thus, the detection of 2,4-DCP from the environment is of great importance. To date, many analytical methods have been established to determine 2,4-DCP, such as UV spectrophotometry [47], high performance liquid chromatography [48,49], gas chromatography [50] and electrochemical methods [51]. However, these methods suffer from high cost, long analysis time intervals, low selectivity, and possible production of secondary pollutants [52]. Therefore, the toxic characteristics and highly hazardous of 2,4-DCP require the development of simple, fast, sensitive, and accurate analytical methods for its detection and quantification.

In this work, we made a first attempt to prepare a highly-controllable core-shell MIPs-based RTP sensor by anchoring a MIPs layer on the surface of SiO₂ nanoparticles with Mn-doped ZnS QDs via a surface molecular imprinting process. The as-synthesized nanomaterials were then used for selective recognition and RTP detection of the target 2,4-DCP. The vinyl modified SiO₂ nanoparticles and Mn-doped ZnS QDs were used as the core substrate and the sensing material, respectively. The uniform imprinted polymer film was grafted onto the surface of vinyl modified SiO₂ nanoparticles by precipitation polymerization. This imprinting layer was obtained also using acrylamide (AM) as the functional monomer, 2,2'-azobisisobutyronitrile (AIBN) as the initiator and ethyl glycol dimethacrylate (EGDMA) as the cross-linker. The characterization, evaluation of optical stability, sensitive and selective of 2,4-DCP were investigated. Finally, this highly-controllable core-shell MIPs-based RTP sensor was demonstrated as a rapid, simple and selective detecting system for selective recognition of 2,4-DCP in real samples.

2. Experimental

2.1. Reagents and chemicals

All chemicals were of analytical grade reagents. ZnSO₄·7H₂O, Na₂S·9H₂O, MnCl₂·4H₂O, ammonia solution (25–28%), tetraethoxysilane (TEOS), 3-(methacryloyloxy)propyltrimethoxysilane (KH-570), acrylamide (AM), ethylene glycol dimethacrylate (EGDMA), 2,2'-azobis(2-methylpropionitrile) (AIBN), 2,4-dichlorophenol (2,4-DCP), 2,6-dichlorophenol (2,6-DCP), 2,4,5-trichlorophenol (2,4,5-TCP) and 2,4,6-trichlorophenol (2,4,6-TCP) were all purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Dry toluene, methanol, ethanol and acetonitrile were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Double distilled water (DDW) was used throughout the experimental procedures.

2.2. Instrument

The structure and morphology of prepared samples were observed by scanning electron microscope (SEM, JEOL, JSM-7001F) and transmission electron microscope (TEM, JEOL, JEM-2100). The X-ray diffraction (XRD) spectra were collected on a XRD-6100Lab X-ray diffractometer (Shimadzu, Japan) with Cu K α radiation over the 2θ range of 10–80°. Infrared spectra (4000–400 cm⁻¹) were recorded using Nicolet NEXUS-470 FTIR apparatus (USA). The phosphorescence measurements were performed on a Cary Eclipse spectrofluorometer (USA) equipped with a plotter unit and a quartz cell (1.0 cm \times 1.0 cm).

2.3. Synthesis and functionalization of SiO₂ nanoparticles and Mn-doped ZnS QDs

SiO₂ nanoparticles were synthesized by the Stöber method [53]. 50 mL of water, 30 mL of ethanol, and 20 mL of ammonia solution

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